



2003 AFCEE Technology Transfer Workshop

San Antonio, Texas

Promoting Readiness through Environmental Stewardship

Source Zone Remediation Using Biodegradation

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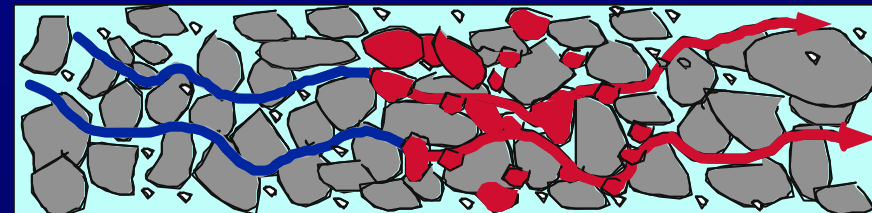
Groundwater Services, Inc.

Feb. 26, 2003

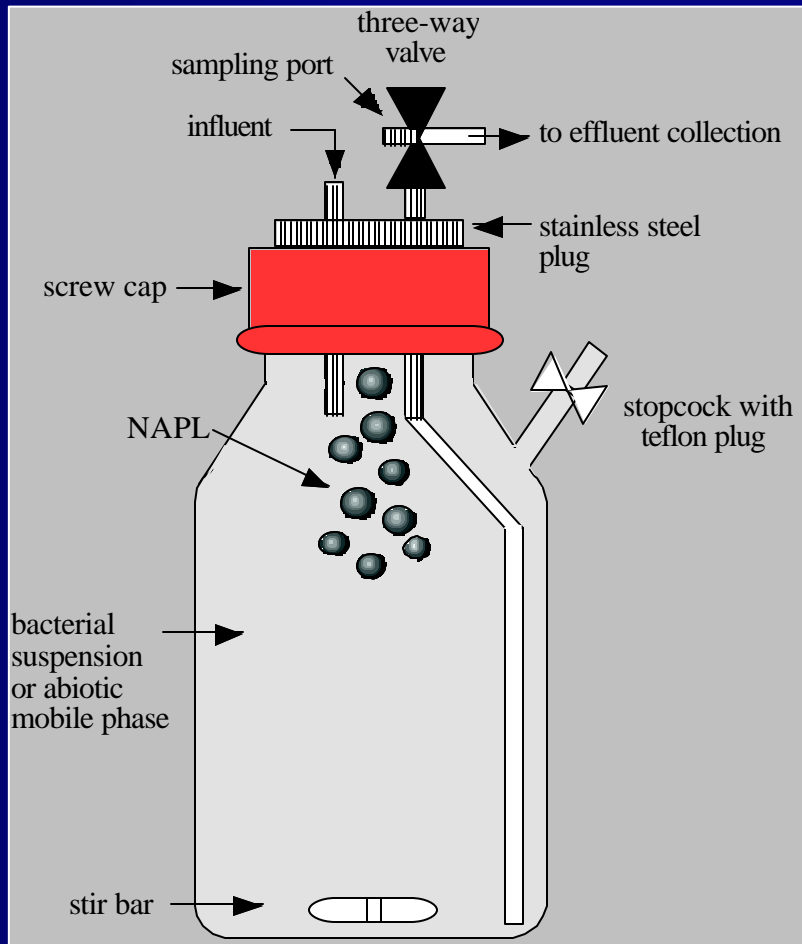
Can You Bioremediate DNAPL Source Zones?

BACKGROUND

- Most chlorinated solvent sites have DNAPL
- DNAPL is rarely seen
- Key issues:
 - cost of substrate
 - how to deliver
 - does mass transfer limitations mean failure?



NAPL Longevity Studies



- Add PCE in tridecane
- Feed formate as E.D.
- Monitor PCE longevity in presence and absence of dechlorination
- Evaluate the impact on “wash out” flux and compositional changes

Summary of Results

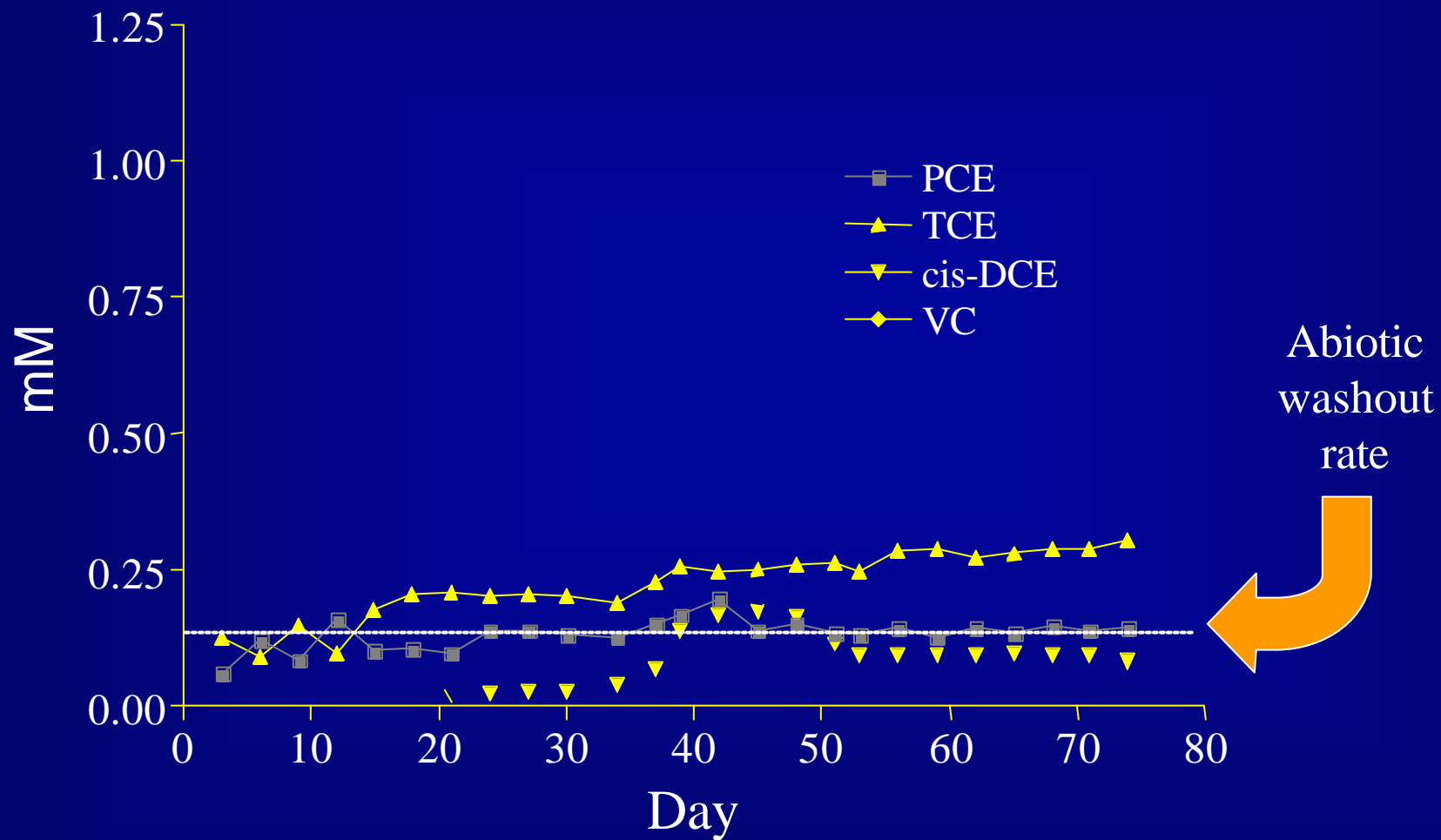
- PCE longevity in biotic systems was **14x faster** than abiotic systems
- Total chlorinated ethenes longevity in biotic systems was **8x faster** than abiotic systems

Carr, Garg, and Hughes (2000) *Environ. Sci. Technol.* 34(6), 1088-1094

Column Studies

- Residual PCE-Tridecane NAPL developed in 3 columns (~ 15%)
- Inoculated with culture and fed pyruvate at 25 mM, 100 mM, and 250 mM
- HRT = 3 days
- Monitored for effluent chlorinated ethenes, methane production, and volatile acids
- Cryogenic dissection after 80 days

Low Electron Donor



Findings

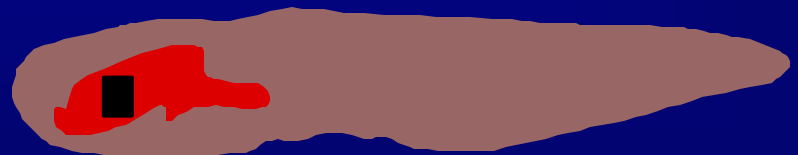
- All columns fermented pyruvate to acetate and propionate, no methane production
- PCE removal was **16x faster** in biotic column fed 100mM pyruvate than dissolution alone
- Total ethene removal was **5.0x to 6.5x greater** than dissolution alone
- Effluent chlorinated solvent concentrations may be poor indicators of longevity

Can You Bioremediate DNAPL Source Zones?

Cost of Substrate

Template Site Economic Analysis (Harkness, 2000)

- Source zone **25m x 30 m x 19 m** (0.2 acres)
- Source contains **2725 kg PCE** (10 drums)
- NAPL saturation = **0.0005** (0.05 % of pore vol.)



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Cost of Substrate

Key Assumptions:

- Need Donor:PCE ratio = **35:1**
- Donor is **\$0.77 per pound**

Case 2: Batch Feed System

- **\$130,000 for donor** (15% of total system cost)

Can You Bioremediate DNAPL Source Zones?

Cost of Substrate

DiStefano and Baral, 2000:

- Donor costs are **\$0.02 to \$0.12 per pound**
- Ratio of donor:PCE ranges from **5x to 20x**
- Cost per pound of PCE: **\$ 0.04 to \$ 0.85**
- **\$1200 for donor** (assuming \$0.20 per lb of PCE)

Can You Bioremediate DNAPL Source Zones?

Delivery Systems

For source treatment, radius of influence is important

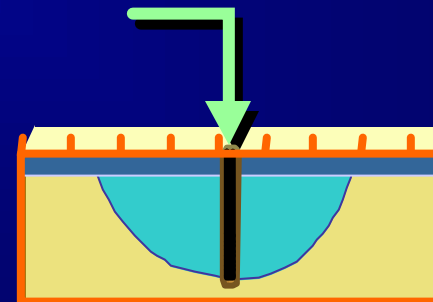
- Dissolved substrates, gas foam: **15 - 30 ft**
- Semi-solids, gas: **10 to 15 ft**
- How many injection points?

<u>Radius (ft)</u>	<u>Wells per Acre</u>
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10	430
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15	200
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30	50
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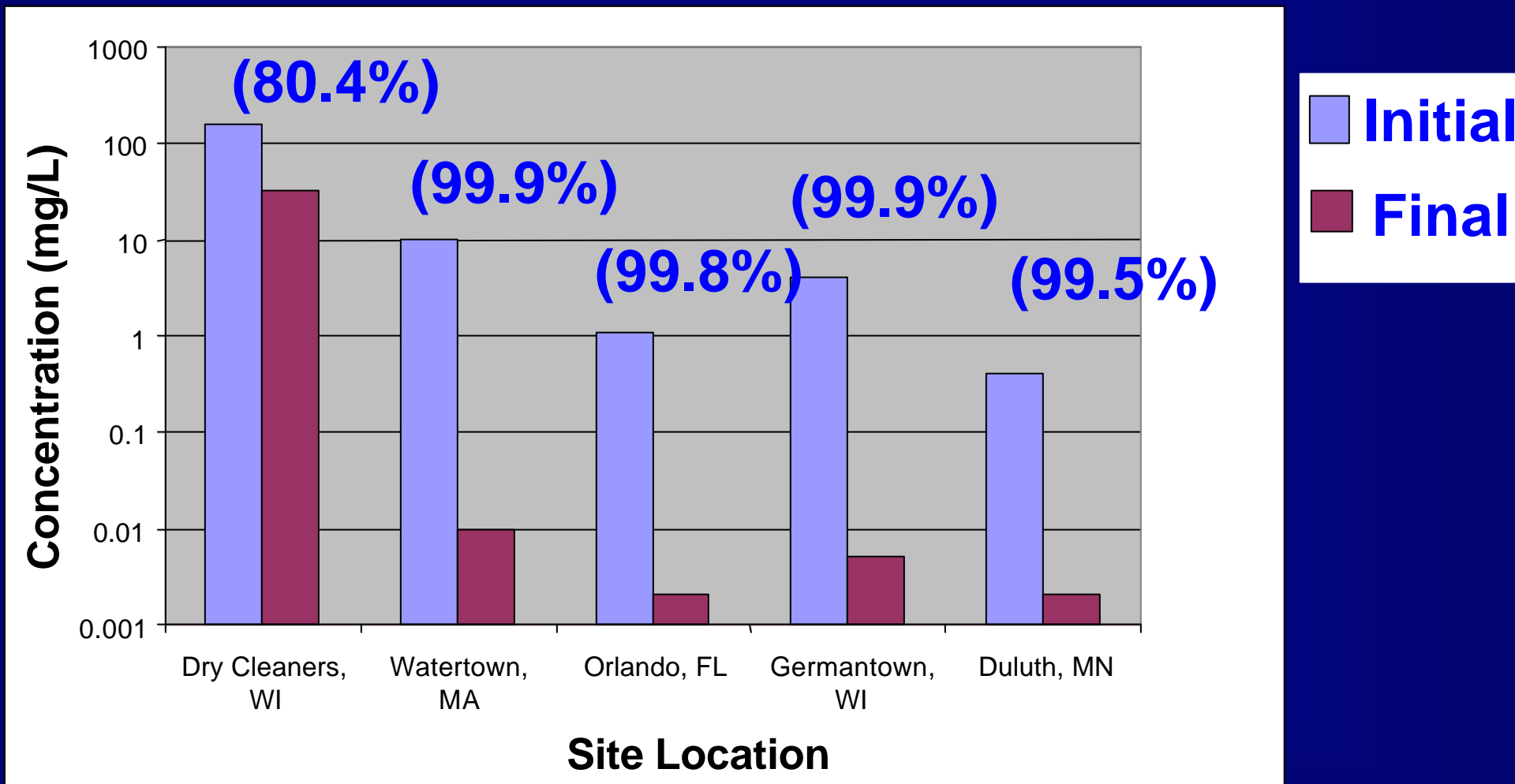


Reported Cost Information for Bioremediation (preliminary)

SITE	TREATMENT	TOTAL COST	TREATMENT AREA	\$ / ACRE
Watertown, MA	HRC	\$ 50 K	0.01 acres	\$ 545 K
Orlando, FL	HRC	\$ 127 K	0.74 acres	\$ 384 K
Duluth, MN	HRC	\$ 20 K	0.05 acres	\$ 436 K
Industrial Site, NJ	HRC	\$ 15 K	0.03 acres	\$ 594 K
Largo, FL	Benzoate, lactate, and methanol	\$ 400 K	0.05 acres	\$ 2500 K
Williamsport, PA	Molasses	\$ 145 K	1.42 acres	\$ 190 K
Idaho Falls, ID	Sodium lactate	\$ 2,360 K	0.72 acres	\$ 3280 K
Houston, TX	Methanol	\$ 700 K	3.33 acres	\$ 210 K

Average Cost ~ \$ 1,000,000 per acre

Reported Decrease in Concentration (mg/L) from SERDP Database

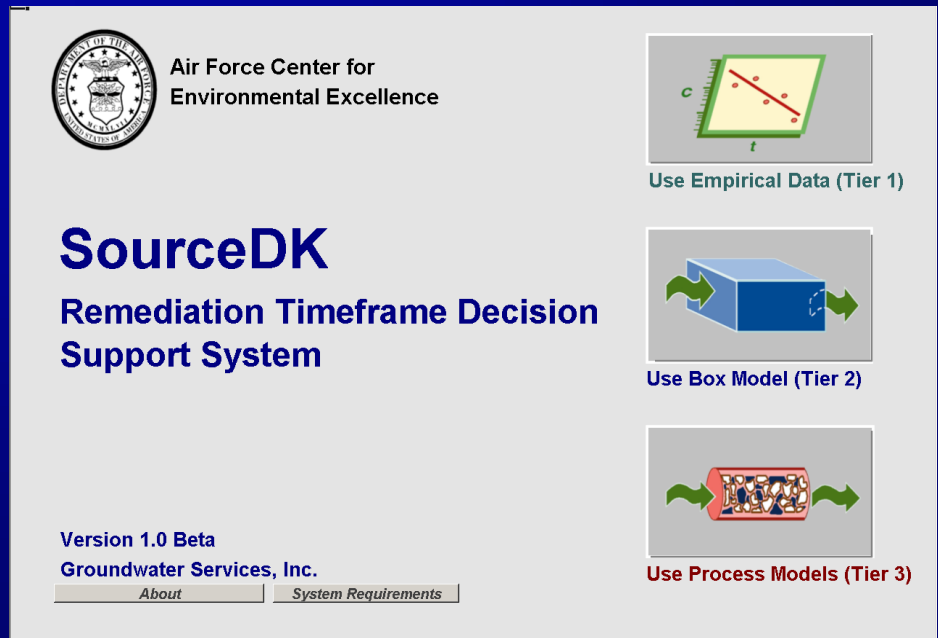



Note: Numbers in () represent the percent reduction (%) in concentration

Can You Bioremediate DNAPL Source Zones?

Mass Transfer Issues - Modeling Analysis

- Modeled Source Decay with SourceDK software
- AFCEE Product in Review



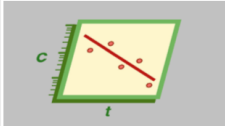
 Air Force Center for
Environmental Excellence

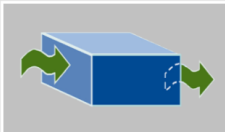
SourceDK

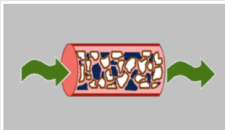
Remediation Timeframe Decision
Support System

Version 1.0 Beta
Groundwater Services, Inc.

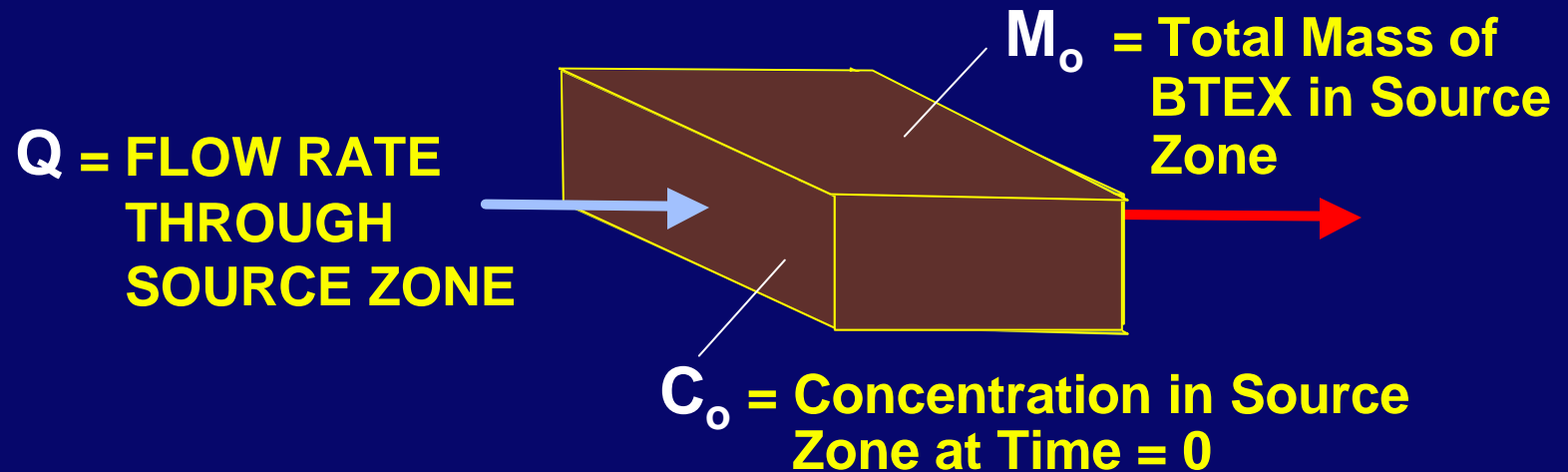
[About](#) [System Requirements](#)


Use Empirical Data (Tier 1)

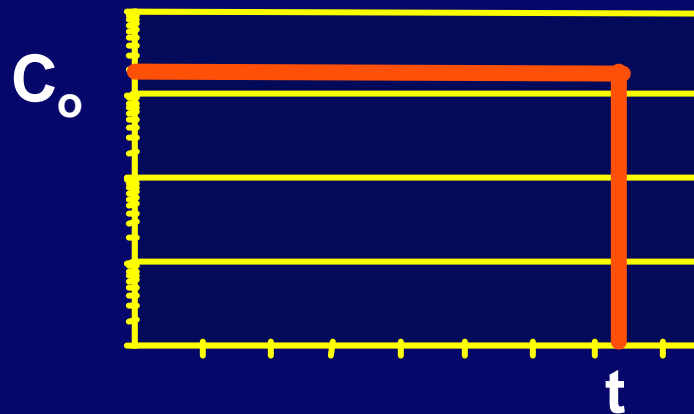

Use Box Model (Tier 2)


Use Process Models (Tier 3)

Approach: Assume Source Zone Is a Box



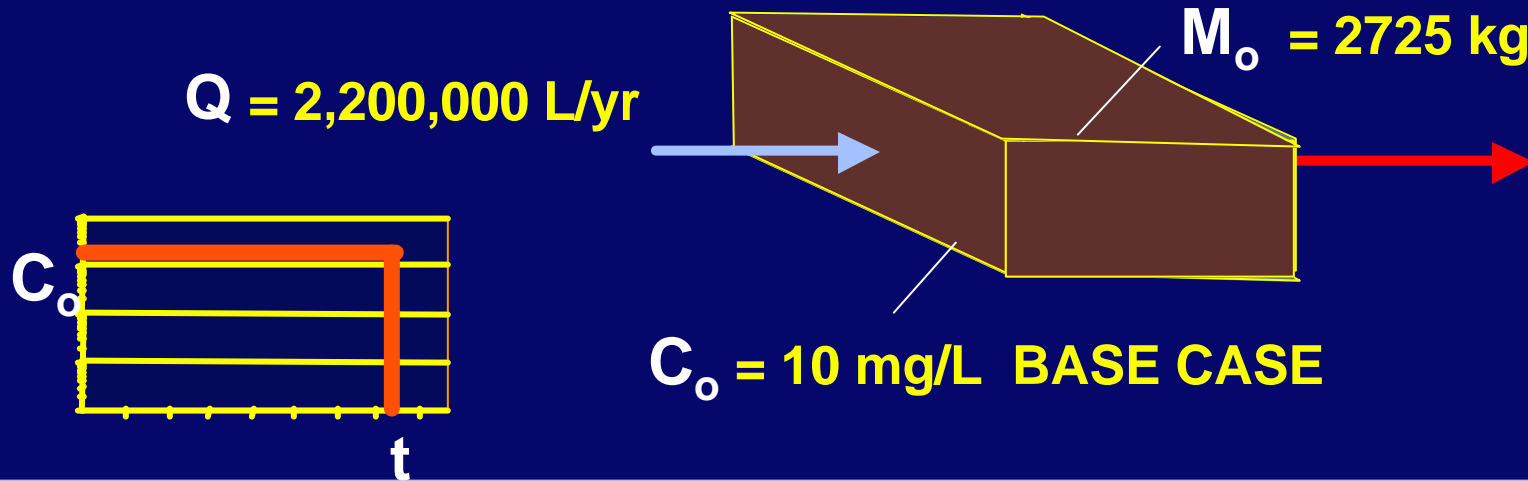
IF CONSTANT SOURCE CONCENTRATION:



$$t = \frac{M_o}{Q C_o}$$

Use Template Site.

Assume Step Function

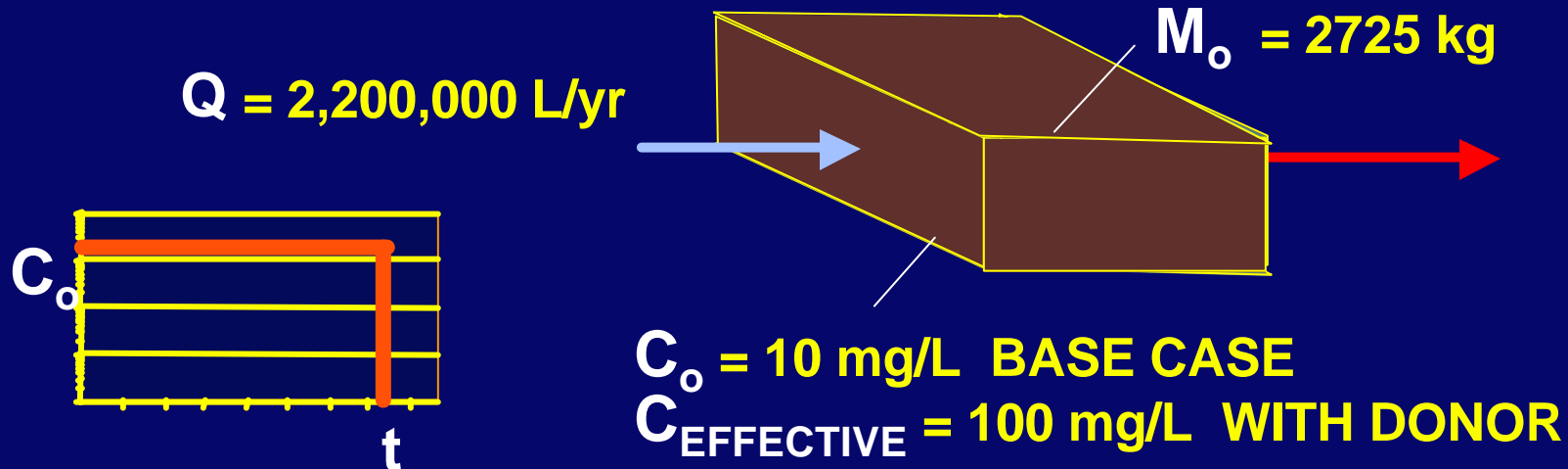


No Biodeg:

$$t = \frac{2725}{(2.2 \times 10^6) (10 \times 10^{-6})} = 124 \text{ yrs}$$

Use Template Site.

Assume donor increases rate by factor of 10x:



No Biodeg:

$$t = \frac{2725}{(2.2 \times 10^6) (10 \times 10^{-6})} = 124 \text{ yrs}$$

With Biodeg:

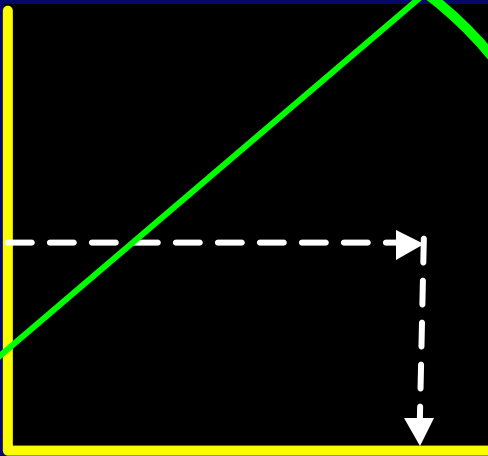
$$t = \frac{2725}{(2.2 \times 10^6) (100 \times 10^{-6})} = 12 \text{ yrs}$$

Better Approximation: Conc. Declines With Tail

First Order Decay Model

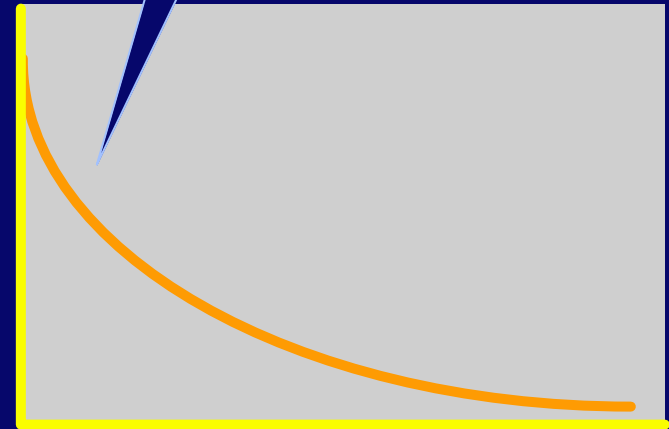
$$C_t = C_o e^{-k_s t}$$

Conc.
in
Source
Zone



time

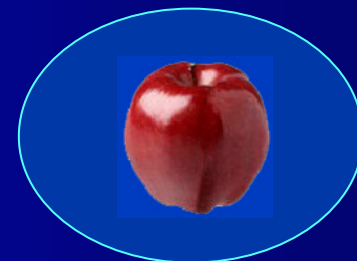
Conc.
in
Source
Zone



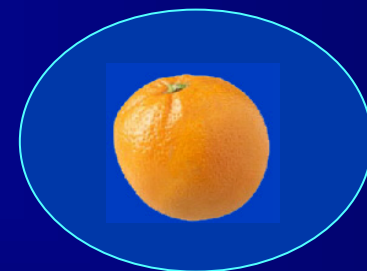
time

Two Different Types of Rate Constants

→ λ represents how quickly dissolved organics are biodegraded (c vs. x)



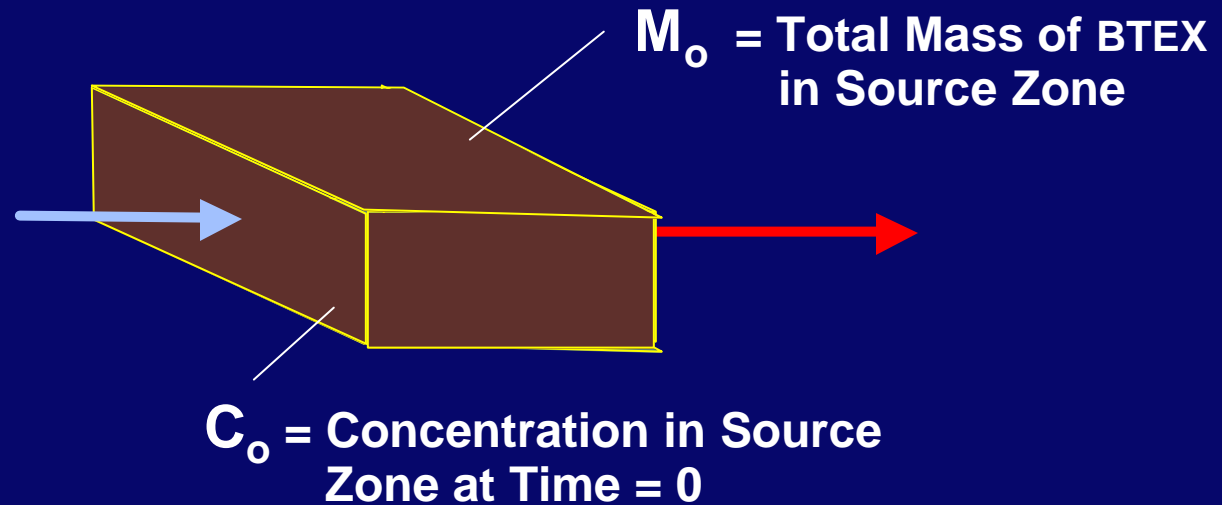
→ k_s represents how quickly source is being dissolved (half-life in years) (c vs. t)



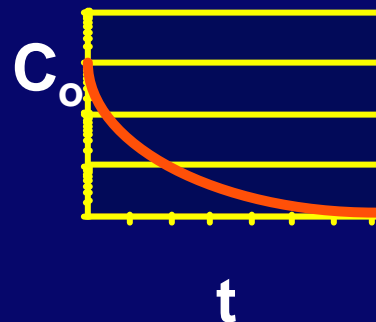
Source: Newell, Rifai, and Wilson, 2003

Example Assuming Declining Source Conc.

**Q = FLOW RATE
THROUGH
SOURCE ZONE**



**IF DECLINING
SOURCE
CONCENTRATION:**

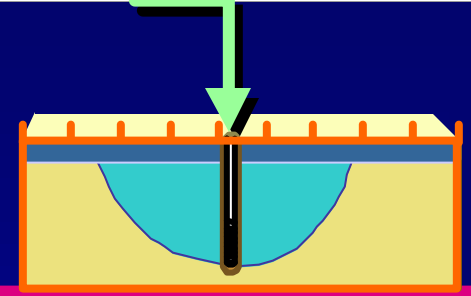


$$k_s = \frac{Q C_o}{M_o}$$

$$C_t = C_o \cdot e^{-k_s t}$$

Can You Bioremediate DNAPL Source Zones?

Rate Analysis



Apply SourceDK model to Template Site

Assume no biodegradation

k_s (per year)

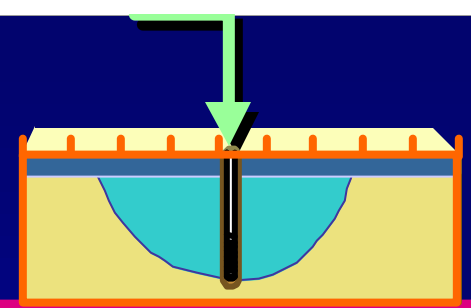
0.008

Time for 99%
Reduction in C

>500 years

Can You Bioremediate DNAPL Source Zones?

Rate Analysis



Can combine k_s and λ



High λ (caused by donor addition) will reduce k_s

SourceDK allows users to see how biodeg affects source lifetime

<u>Lambda (per yr)</u>	<u>k_s (per year)</u>	<u>Time for 99% Reduction in C</u>
1	0.03	176 years
10	0.2	24 years
100	2	3 years

Can You Bioremediate DNAPL Source Zones?

Are These Rates Reasonable?

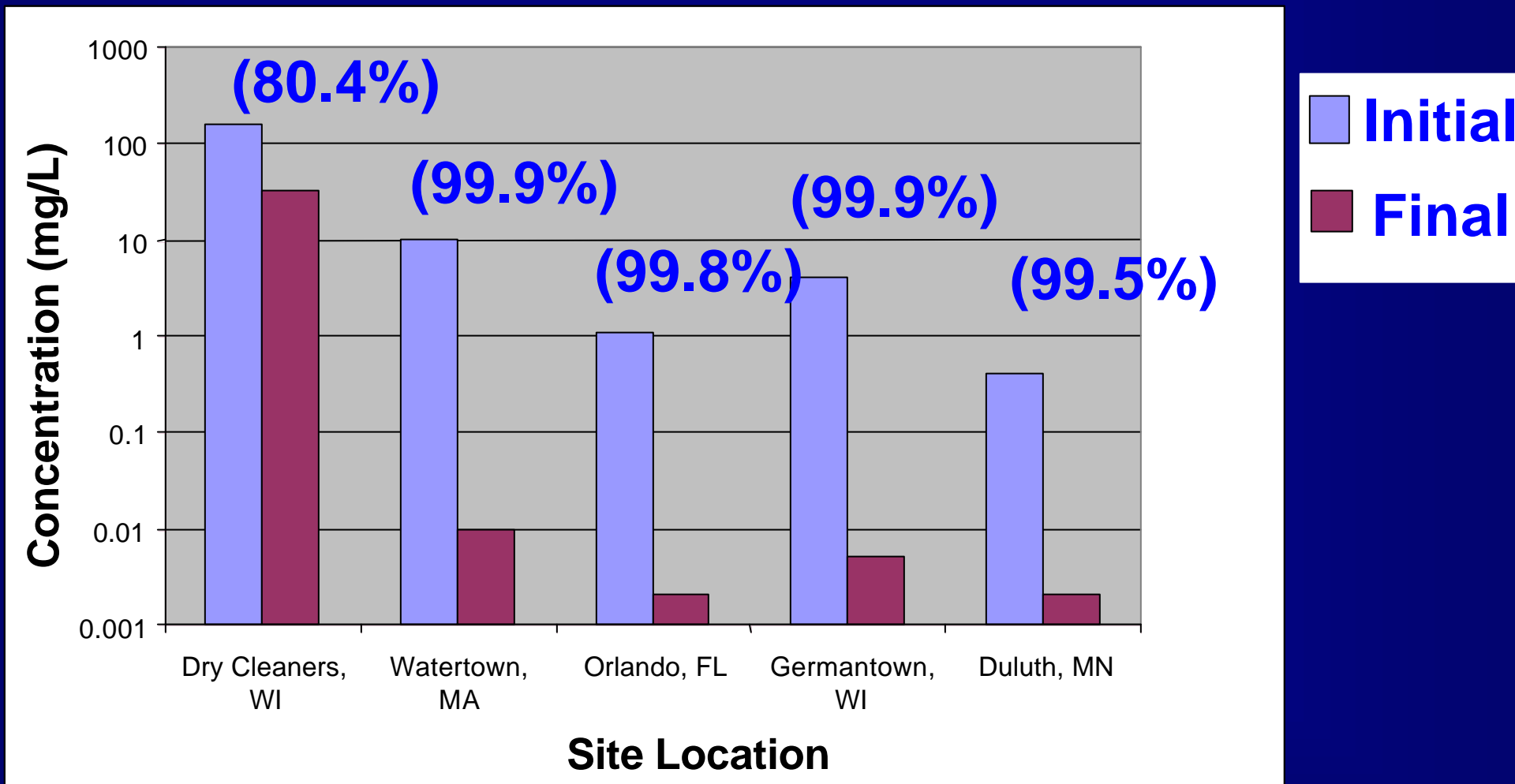
	<u>Lamba (per yr)</u>	<u>k_s (per year)</u>	
	1	0.02	
	10	0.2	
	100	2	
	70 - 200 (<i>SERDP for H₂</i> <i>addition</i>)	0.5 - 5 (<i>Aziz et al, 2000 for</i> <i>typical MNA sites</i>)	
Reported Rates			

Can You Bioremediate DNAPL Source Zones?

Are These Rates Reasonable?

It is reasonable to expect that high source decay rates can be achieved at source bioremediation sites.

Reported Decrease in Concentration (mg/L) from SERDP Database



Note: Numbers in () represent the percent reduction (%) in concentration

Can You Bioremediate DNAPL Source Zones?

CONCLUSION

- Cost data suggests donor cost relatively small
- **Cost of delivery system more important**
- Rate data from lab, models indicates that bioremediation is feasible for treating source zones **in some source settings**
- **Literature data shows some successes**
- Cost vs. containment key issue